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FINAL REPORT
Experimental and Theoretical Studies of Molecular Dynamics
AFOSR CONTRACT 81-00298

Principal Investigator - Stuart A. Rice

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Period: October 1, 80 to September 30, 1982

During the period to which this report refers, significant progress was made in both experimental and theoretical studies of intramolecular and intermolecular dynamics. A more detailed description of the work accomplished will be found in the abstracts of the papers listed. The highlights of our work include.

1. Completion of combined experimental and theoretical studies of very low energy collision induced vibrational relaxation;
2. Further development of the relationship between large amplitude motion and the onset of chaos;
3. Definitive testing and verification of the interpretation of nonexponential time evolution of an excited state of a molecule with intermediate case level structure, including a demonstration of the role of rotational states in defining the rate of the radiationless process.

In addition, useful results were obtained in our studies of radiationless processes and of "room temperature" collision induced vibrational relaxation of electronically excited polyatomic molecules.

The following are abstracts of the papers published or accepted for publication.

1. Very Low Energy Collision Induced Vibrational Relaxation.

Mode Dependent Enhanced Vibrational Relaxation in Low Energy He-¹B₂ Aniline Collisions, James Tusa, Mark Sulkes and S.A. Rice. J. Chem. Phys. 73, 5897 (1980).

We have discovered that very low energy collisions of helium with aniline exhibit both large cross section for vibrational relaxation and selectivity of

the pathway of relaxation. A model based on scattering resonances is proposed to interpret these results.

Atom-Diatomic Molecule Collisions at Very Low Energies. 1. A Computational Study of the Adiabatic and Effective Potential Approximations, J. Chem. Phys. 85, 3187 (1981), V. Sethuraman and S.A. Rice

As a preliminary step in the study of rovibrational scattering of atoms and molecules at very low energies ($1-100 \text{ cm}^{-1}$), we examine the usefulness of the adiabatic (LZCES) and effective potential (EP) approximations in the description of these collisions. He-, Ne-, and Ar-I₂ collisions, in the rigid-rotor approximation, are examined here to determine the behavior of the low-energy limit of scattering and the range, depth and anisotropy of the potential over which the LZCES and EP approximations yield useful results. The adiabatic approximation is found to be valid for energies greater than 1.5, 5, and $\sim 20 \text{ cm}^{-1}$, respectively for He, Ne and Ar projectiles and is observed to break down with increasing range and anisotropy of the potential. The effective potential approximation is observed to be valid for energies greater than $\sim 3 \text{ cm}^{-1}$ for He and Ne, and its accuracy is noted to be much less sensitive to the collision energy, mass of the projectile, and parameters of the potential in comparison with the adiabatic approximation.

Mode-to-Mode energy transfer in $^1\text{B}_2$ aniline induced by very low energy collisions with He, J. Chem. Phys. 76, 3513 (1982), James Tusa, Mark Sulkes, Stuart A. Rice and Christophe Juvet

Collision induced vibrational relaxation of selected single vibronic levels of $^1\text{B}_2$ aniline has been studied for the collision energy range $\sim 1-100 \text{ cm}^{-1}$. We find that very low energy collisions with He lead to efficient and selective mode-to-mode energy transfer, with the collision energy required for efficient relaxation varying with the nature of the initial vibrational excitation. This dependence on initial vibrational state is consistent with the orbiting resonance model of the collision previously proposed.

Further Evidence for Enhanced Vibrational Relaxation Induced by Very-Low-Energy Atom-Polyatom Collisions, Chem. Phys. Letts. 84, 241 (1981), Christophe

Jouvet, Mark Sulkes and Stuart A. Rice

Very-low-energy ($<20 \text{ cm}^{-1}$) collisions of He with $^1\text{B}_2$ fluorobenzene have very large, mode-dependent, vibrational relaxation cross sections, whereas similar collisions of He with $^1\text{B}_{2u}$ benzene have vanishingly small cross sections. These data are consistent with a scattering resonance model for very-low-energy collision-induced vibrational relaxation.

Very Low Energy Collision Induced Vibrational Relaxation of $^1\text{A}_u$ Glyoxal, J. Chem. Phys. (in press) Christophe Jouvet, Mark Sulkes and Stuart A. Rice

We report the results of a study of very low energy collision induced vibrational relaxation of $^1\text{A}_u$ glyoxal. The observed pathways of relaxation are interpreted using a previously proposed orbiting resonance model for the He: glyoxal collisions. It is inferred that (i) single collision-single quantum transfers dominate the relaxation process, and (ii) when there are near degeneracies in the vibrational manifold the lowering of symmetry in the orbiting resonance can permit mode mixing that is prohibited in the isolated molecule.

Atom-Molecule Collisions at Very Low Energies: A Correlation Function Approach, J. Chem. Phys. (in press) Charles Cerjan, Michael Lipkin and Stuart A. Rice

An extension of the neutron diffraction formalism to low energy atom-molecule scattering including all recoil effects is presented. The nature of the atom-molecule interaction suggests that the diffraction model should be qualitatively correct in the low collision energy regime for vibrational relaxation. The customary impulsive collision assumptions which lead to the use of the Born approximations are replaced by more general transforms which account for possible distortion of the wave function by the potential. Model calculations for a simple vibrational de-excitation process are given.

Comparison of Vibrational Relaxation of $^1\text{A}_u$ Glyoxal Induced by Very Low Energy Collisions and by Photodissociation of van der Waals Complexes, Chem. Phys. Letts. (in press) Mark Sulkes, Christophe Jouvet and Stuart A. Rice

We report a comparison of the energy redistributions accompanying very low energy collision induced vibrational relaxation of $^1\text{A}_u$ glyoxal and photodissociation of the corresponding van der Waals complex.

A Theoretical Analysis of Very Low Energy Collision - Induced Vibrational Relaxation in the System He-I₂(³π_{o+u}), J. Chem. Phys. (in press) Charles Cerjan and Stuart A. Rice

Vibrational de-excitation in the low energy collisions of He with I₂ (³π_{o+u}) is examined within the close-coupled scattering formulation using a sum of pairwise Morse interactions to describe the potential surface. Cross sections for zero total angular momentum are given as a function of energy for various rotational and vibrational transitions with the I₂ molecule prepared in the n=25 vibrational state. Similar results for total angular momentum of 2, 1 and 0 are also reported for the n=1 initial state of I₂. These calculations are in general agreement with the known experimental results and support the arguments advanced previously to explain the unexpectedly large observed relaxation cross section.

Very Low Energy Collision Induced Rotational Relaxation: A Theoretical Analysis, Chem. Phys. Letts. (in press) V. Sethuraman, C. Cerjan and Stuart A. Rice

Rotational relaxation induced by very low energy collisions is examined within a closed-coupled scattering formalism. Three dimensional quantum mechanical calculations, which employ a sum of pairwise Morse interactions to model the potential surface, are reported. A vibrationally averaged potential is assumed to be a valid description of this system, so that rotational effects are thereby decoupled from vibrational processes. Total cross sections for elastic and inelastic processes are given as a function of increasing translational energy for three different Morse parameter choices. The trends seen in the calculations support the experimental observations for rotational relaxation in the I₂-rare gas systems studied by Tusa, Sulkes and Rice.

2. Chaos and Large Amplitude Motion

A Comment on Dynamical Chaos in Classical and Quantum Mechanical Hamiltonian Systems, To appear in Proceedings held in Germany, Plenum Press, Stuart A. Rice

The work reviewed in this article is essentially the same as that of the

following two abstracts:

An extension of the concept of Kolmogorov entropy to quantum mechanical systems is given. Using the Kolmogorov entropy as a common basis for discussion, the onset of chaotic motion in classical mechanical and quantum mechanical systems is compared. It is found that if the spectrum of the system is discrete, the Kolmogorov entropy is zero, and therefore that a bounded quantum mechanical system cannot have chaotic motion like that observed for a corresponding classical mechanical system. This analysis leads to the prediction that if the distributions of states are similar for two bounded systems which in the classical limit have, respectively, quasiperiodic and chaotic motion, wave packets for the two systems decay at similar rates as found by Brumer and Shapiro. The relationship between the defined Kolmogorov entropy, previous interpretations of "KAMlike" onset of chaos in quantum mechanical systems, and the role played by preparation and observation of a system in influencing the intramolecular dynamics, are discussed.

An improved local criterion is proposed for the onset of dynamical chaos in a classical mechanical Hamiltonian system. This criterion is based on the observation that it is only neighboring trajectories which diverge in the direction perpendicular to the flow in phase space that contribute to chaotic motion. The necessary condition for such divergence of neighboring trajectories is the existence of a region where the curvature of the potential energy surface perpendicular to the trajectory is negative. It is shown, for the Henon-Heiles model system, that the lowest critical energy for the onset of chaos is the same as obtained from the Brumer-Duff-Toda-Corjan-Reinhardt criterion, but that the regions of prescribed negative curvature are only a small fraction of the accessible energy surface. Consequently, the BDTCR criterion for onset of chaotic motion is augmented by the condition that the trajectory cross the critical locus in a manner which permits penetration of one of the regions where the surface curvature is negative perpendicular to the trajectory. Given that the regions of local instability are only a fraction of the accessible energy surface, the relationship between local instability and globally dynamical chaos is discussed, and a mapping of the trajectory into a macrostate occupation number representation proposed. That mapping is used to generate an upper bound for the Kolmogorov entropy of the system. The upper bound so obtained is only close to the Kolmogorov entropy

when the sequential occupation of macrostates by a trajectory consists of successive uncorrelated transitions. For the Henon-Heiles model it is shown that correlation in macrostate occupation along a trajectory is long lived, so that even when there is dynamical chaos on the long time scale there can be quasiperiodic motion on the short time scale. The relationship of the new results to the characterization of intramolecular energy transfer is briefly discussed.

Is Dynamical Chaos the Same Phenomenon in Classical and Quantum Mechanical Hamiltonian Systems? J. Phys. Chem. 86, 2153 (1982) Stuart A. Rice and Ronnie Kosloff

A brief discussion of the Kolmogorov entropy interpretation of classical mechanical chaos and quantum mechanical chaos is given. It is pointed out that if a quantum mechanical Kolmogorov entropy is constructed to be analogous to a classical mechanical Kolmogorov entropy, then, for the case that the spectrum of the quantum mechanical system is discrete, the Kolmogorov entropy vanishes and there is no chaos, irrespective of the behavior of the corresponding classical mechanical system. A simple model which illustrates the deviation between classical and quantum dynamics with respect to chaos is also discussed.

Some Properties of Large Amplitude Motion in an Anharmonic Chain with Nearest Neighbor Interactions, J. Phys. Chem. 77, 2607 (1982) Michael A. Collins and Stuart A. Rice

We consider the classical and semiclassical dynamics of a one-dimensional atomic lattice with periodic boundary conditions. Using quasicontinuum approximations, we derive the form of the perfectly periodic vibrational modes of the chain for a cubic and a Lennard-Jones nearest neighbor interaction potential. These long wavelength traveling waves are trains of solitons, rather than harmonic modes, even at low energy. A semiclassical quantization procedure is used to obtain the energy level spectrum for a model anharmonic Xe lattice. The lower eigenenergies are near the harmonic values even though the corresponding classical motion is solitonlike. We show that at high energy the soliton character of the vibration leads to a breakdown in their stability. This is related to the onset of classical chaos.

Further Comments Concerning Large Amplitude Motion in an Anharmonic Chain with Nearest Neighbor Interactions, submitted to J. Chem. Phys., Steven Bradlow, Michael A. Collins and Stuart A. Rice

We present an extension of some numerical studies, of Collins and Rice, on large amplitude motion in an anharmonic chain with nearest neighbor interactions. In particular, the effect of the anharmonicity in the pair potential on small wavenumber modes is examined up to their fifth excited state. The extended energy spectra are found to reveal no new trends and the observations of Collins and Rice concerning the impact of the nonlinearities in the system on mode energies and waveforms are seen to remain valid.

3. Radiationless Decay in Intermediate Case Level Structure Molecules

Intermediate Case Radiationless Decay: The Excited State Dynamics of Pyrazine, Chem. Phys. 60,335 (1981), Daniel b. McDonald, Graham R. Fleming and Stuart A. Rice

This paper reports new measurements of the non-exponential fluorescence decay of pyrazine, covering the time range 0.1-100 ns. The results of our measurements remove the inconsistencies between experiment and the Frad-Lahmani-Tramer-Tric model of the radiationless decay in this molecule. In particular, our data show that the triplet component of the mixed singlet-triplet levels does increase with increasing triplet density of states. The effective density of triplet levels determined from our experimental data exceeds the theoretical density of vibrational levels. We propose that at the excitation levels achieved in the triplet manifold there is extensive scrambling of rotational states, but that conservation of nuclear spin states permits a level with total angular momentum quantum number J to couple to only $(2J+1)/4$ of the $2J+1$ rotational levels built on one vibration. The appropriate theoretical density of states to be compared with experiment is then obtained by multiplying the vibrational density of states by $J/2$. Good agreement is found between experimentally determined and calculated densities of states.

4. Other Research

Rotational Analysis of Bands at the Long-Wavelength End of the $A^2A_2 - X^2B_1$

Electronic Transition of ClO_2 , J. Molecular Spectroscopy 36, 499 (1981) Y. Hamada, A.J. Merer, S. Michielsen and S.A. Rice

The rotational structures of the longest wavelength bands of the $A^2A_2-X^2B_1$ electronic transition of ClO_2 have been investigated from high-dispersion plates taken with separated ClO_2 at dry ice temperature. Complete analyses have been obtained for the 000-000 and 002-000 bands, and partial analyses have been obtained for the 010-000 band and bands of the $(v_1=1-5)$. The levels of the $(v_1=0)$ series are all perturbed, more or less strongly, by vibrational Coriolis effects within the A^2A_2 state. The centrifugal distortion constants and the inertial defect of the zero-point level, together with the positions of the Coriolis perturbations, show that the antisymmetric stretching fundamental of the A^2A_2 state lies near 426 cm^{-1} ; since the overtone level of this vibration is observed at 1583 cm^{-1} there is strong evidence for a double minimum potential function in the Q_3 coordinate of the A^2A_2 state, with barrier height about 1250 cm^{-1} . The upper state geometric structure for the symmetrical configuration is $r(\text{Cl-O}) = 1.6270\text{ \AA}$, $\angle\text{O-Cl-O} = 106.18^\circ$. An interesting variation of the predissociation linewidths with K and the spin state has been found: for all vibrational levels of the upper state that can be analyzed the F_1 spin component levels ($N=J-1/2$) are wider than the F_2 levels ($N=J+1/2$), and the difference in width becomes larger with decreasing K so that the F_1 components lines are essentially missing below $K=4$ even though the F_2 component lines remain comparatively sharp.

Intersystem Crossing in Cold Isolated Molecules of Naphthalene, J. Chem. Phys. 75, 5672 (1981), Fred M. Behlen and S.A. Rice

We report the results of an extensive study of the rate of radiationless decay in very cold, isolated, naphthalene molecules. The experimental method employed, namely, pulsed narrow band laser excitation of a pulsed seeded supersonic free jet, avoids the complications imposed by the sequence congestion generated by the thermal excitation characteristic of ordinary vapor samples. Our analysis of the fluorescence decay includes a method for transforming room temperature quantum yield data to quantum yields characteristic of the molecules in the supersonic free jet. It is concluded that (a) the out of plane vibration $2(b_{2g})$ is very likely a promoting mode for intersystem crossing; (b) there is no need to invoke near resonant coupling of levels in the prepared singlet and final triplet manifolds to explain features

of the radiationless decay; and (c) in general, the broad features of radiationless decay in naphthalene are very much like those of the corresponding decay in benzene, and can be similarly explained.

Fluorescence Spectroscopy of Cold and Warm Naphthalene Molecules: Some New Vibrational Assignments, J. Chem. Phys. 75, 5685 (1981) Fred M. Behlen, Daniel B. McDonald, V. Sethuraman, and Stuart A. Rice

The fluorescence excitation spectrum of naphthalene seeded in a supersonic free jet and the single vibronic level fluorescence spectrum of room temperature naphthalene vapor have been used to determine assignments for a number of combination and sequence transitions that were previously unassigned. Our data, when combined with data in the literature, require some changes in previous assignments. The spectroscopic literature on naphthalene and naphthalene- d_8 is reviewed and up-to-date tables of vibrational frequencies are presented.

Collision Induced Intramolecular Energy Transfer: The He- 1B_2 Aniline System J. Chem. Phys. 75, 1046 (1981), Stewart M. Cameron, Mark Vandersall and Stuart A. Rice

Previous reports from this laboratory have dealt with collision induced vibrational energy redistribution in 1B_2 aniline under gas bulb conditions; the collision partners used were Ar, CH_3F , and H_2). As a complement to the study of intramolecular relaxation induced by very low energy He- 1B_2 aniline collisions, we have also examined this relaxation process at room temperature.

Theoretical and Experimental Characterization of Supersonic Expansions from Slit Sources, Chem. Phys. 87, 515(1982), Mark Suikes, Christophe Couvet and Stuart A. Rice

Theoretical and experimental studies of supersonic expansions from slit sources are reported.

PROJECT SUMMARY

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Period: October 1, 1980 to September 30, 1982

Title: Experimental and Theoretical Studies of Molecular Dynamics

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